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RELATIVE IMPORTANCE OF VARIOUS SOURCES OF DEFECT-PRODUCING HYDROGEN INTRODUCED INTO STEEL DURING APPLICATION OF VITREOUS COATINGS

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National Bureau of Standards

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SUMMARY

When porcelain enamels or vitreous-type ceramic coatings are applied to ferrous metals, there is believed to be an evolution of hydrogen gas both during and after the firing operation. At elevated temperatures rapid evolution may result in blistering while if hydrogen becomes trapped in the steel during the rapid cooling following the firing operation gas pressures may be generated at the coating-metal interface and flakes of the coating literally blown off the metal. This latter type of defect is known as fishscaling.

Although the behavior of hydrogen in the coating-steel system has received considerable study, the relative importance of the different possible sources of the hydrogen causing the defects has been principally a matter of conjecture. To determine experimentally the relative importance of the principal sources, a procedure was devised in which heavy hydrogen (deuterium) was substituted in turn for regular hydrogen in each of five possible hydrogen-producing operations in the coating process. The gas that was evolved when the coated steel specimens fishscaled after firing was collected and analyzed with the mass spectrometer. The content of the deuterium isotope in the total hydrogen gas evolved was then taken as a measure of the relative importance of the source under study.

The findings of the study were as follows:

(1) The principal source of the defect-producing hydrogen was the dissolved water present in the enamel frit that was incorporated into the coating. This water apparently reacts with the steel at elevated temperatures, releasing atomic hydrogen, some of which is dissolved by the steel. During fast cooling the steel becomes supersaturated with respect to hydrogen and the atomic hydrogen slowly diffuses to the interface where it collects in minute cavities or fissures, forming molecular hydrogen. This movement is irreversible and sufficient pressure builds up to cause fishscaling in the coating layer.

(2) The acid pickling, the milling water, the chemically combined water in the clay, and the quenching water were all minor sources of defect-producing hydrogen under the test conditions used.

Confirming experiments showed that fishscaling could be eliminated by using a water-free coating. Efforts to produce a water-free frit, or glass, by using dehydrated raw materials in conjunction with electric-furnace smelting and water-free quenching showed that such a method has promise.

Other experiments indicated that reboiling (the blistering of a vitreous coating when reheated after the first firing) was also related to the dissolved water in the coating layer.

INTRODUCTION

Several investigations, especially over the past decade, have established that hydrogen is a major cause of coating defects when porcelain enamels are applied to a steel base (references 1 to 3). There has, however, been considerable uncertainty and difference of opinion as to the major source or sources of the defect-producing hydrogen.

The purpose of the present investigation was to study the possible sources and to evaluate their relative importance. With such information available it was believed likely that methods or procedures could be devised whereby coatings free of hydrogen defects[1] might consistently be obtained. It was also believed likely that the results obtained with porcelain enamel on steel would be applicable when vitreous-type ceramic coatings are applied to steel and to the so-called low-strategic alloys. Because of this connection with ceramic coatings and the growing importance of ceramic coatings to the aircraft industry, the investigation as herein described was performed as a part of a broad study on ceramic coatings being conducted at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

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[1]Coating defects that have been ascribed to hydrogen include fishscaling, primary boiling, reboiling, and blistering. Fishscaling is a localized fracture of the coating glass caused by excessive gas pressure at the coating-metal interface. Primary boiling is the rapid bubbling of the enamel layer during the early stages of firing caused by the escape of entrapped and evolved gases, while reboiling is the blistering at about 1050° F of a vitreous coating when it is reheated after the first firing.

The authors gratefully acknowledge the valuable assistance of the Mass Spectrometry Section of the National Bureau of Standards, under the direction of Dr. F. L. Mohler, for performing the mass-spectrometer analyses.

POSSIBLE SOURCES OF HYDROGEN IN ENAMELING PROCESS

Some hydrogen is usually present in the steel as received and additional hydrogen may be introduced at several stages of the enameling process. The first and most obvious source is the acid-pickling operation. During this treatment the acid reacts with the steel and part of the hydrogen thus formed may be readily occluded by the metal (reference 4).

The second possible source of hydrogen is a reaction of iron in the steel with any water that may be present in the enamel layer during the firing operation. When iron is heated to enameling temperature in the presence of steam the following reaction takes place (reference 5):

$$Fe + H_2O \longrightarrow FeO + H_2$$

This reaction would proceed as shown if the hydrogen were continuously removed from the system. Such removal could occur in the enamel-metal system either by escape of the hydrogen through the enamel layer or by solution into the steel. If it passes into the steel, it then becomes capable of producing enamel defects.

The water that might come in contact with the hot steel during the firing operation could conceivably originate from one or more of the following sources:

(1) The water vapor that might be present in the furnace during firing

(2) The water used for milling and suspending the enamel slip

(3) The chemically combined water in the clay used for suspending the enamel slip

(4) The dissolved water in the frit

The water dissolved in the frit could, in turn, be derived from: (a) The water present in the batch materials, (b) the water present in the atmosphere of the smelting furnace, and (c) the water used in quenching the molten glass to form the small friable frit particles.

Some attention was given to all of the above-mentioned sources, but the effect of the water vapor present in the atmospheres of the smelting and enameling furnaces and the effect of water present in the raw batch materials used for preparing the frit were not studied by tracer techniques.

USE OF DEUTERIUM (HEAVY HYDROGEN) AS A TRACER

Deuterium is an isotope of hydrogen. It differs from protium (ordinary hydrogen) in that its nucleus contains a neutron as well as a proton whereas protium contains a proton only. Because of the difference in mass (deuterium, 2; protium, 1) the two isotopes can be readily separated with the mass spectrometer and, by using the proper techniques, the relative amounts of each that are present in any given sample can be determined quantitatively. Deuterium and protium have almost identical chemical properties and their physical properties are similar. Thus, deuterium can be used as a tracer in many reactions. The solubility of deuterium in iron has been determined by Sieverts, Zapf, and Moritz (reference 6). These data are plotted in figure 1.

In the present study, deuterium in the form of heavy water (D_2O) was substituted, in turn, for ordinary water (H_2O) in each of five different processes that are related to enameling operations. The gases given off when the resulting coated specimens fishscaled were collected and analyzed with the mass spectrometer. The percentage of deuterium in the hydrogen gas was then computed and this figure was taken as a measure of the importance of that particular source in producing hydrogen defects in the enamel coating. The methods used for substituting heavy water for regular water in the various operations are given in the section entitled "Methods of Introducing Heavy Water." The procedure used for collection of the gases during fishscaling and their subsequent analysis is given in the section "Test Equipment and Procedure."

MATERIALS

The deuterium oxide, which was obtained from a commercial source, contained 99.8 percent heavy water and 0.2 percent ordinary water. It was received in 100-gram sealed flasks.

Two steels were used in the principal part of the study. Steel A was 18-gage enameling iron while steel B was a 10-gage low-carbon steel that had given considerable trouble from delayed fishscaling in one enameling plant. In addition a titanium-bearing, low-carbon, 18-gage steel was used in a few experiments. This latter steel (steel C) is purported to have low susceptibility to hydrogen and it has been demonstrated (reference 7) that it tends to minimize defects when used as a base for application of porcelain enamels.

The chemical analyses of the three steels are given in table 1 and the determined gas contents before the enameling treatment are

presented in table 2. Table 3 gives the batch and oxide compositions of the ground-coat enamel frit (109-0) used for most of the experiments. This frit was selected from an earlier study (reference 8) as being suitable for the preparation of a single-frit enamel ground coat. The 109-0 frit is the same as the frit E described in reference 8 except that the 109-0 contains no adherence oxides. The clay used in preparing the ground-coat enamel slips was a commercial grade of Florida kaolin.

TEST EQUIPMENT AND PROCEDURE

A schematic drawing of the collection cell, with heater, is shown in figure 2. Two cells of this type were used, one having a volume at 20° C of 152.3 cubic centimeters and the other, 173.3 cubic centimeters.

The mass spectrometer was of the type described by Washburn, Wiley, Rock, and Berry (reference 9).

A standardized test procedure was used in each experiment for preparation of specimens, collection of gases given off during fish-scaling, and analysis of the gas sample with the mass spectrometer. This procedure may be summarized as follows:

Before beginning a given experiment, 10 steel specimens, 2 inches by 3/4 inch, were selected at random from a large supply that had been sheared from the same sheet. (In the case of specimens of steel B, which were of greater thickness, five specimens were used.) These specimens were degreased in an organic solvent and then pickled for 10 minutes in 5 percent by weight of sulphuric acid maintained at a temperature between 156° and 159° F. After removal from the acid the specimens were rinsed in hot tap water for 1 minute and then dried at 212° F for 15 minutes. Immediately after cooling to room temperature the specimens were coated by dipping in a slip (less than 48 hr old) of the E-1 coating that contained:

Constituent	Content (grams)
Frit 109-0	200
Florida kaolin	10
Water	85

and that was prepared in the following manner:

Milling time in 1-quart jar mill, hr	$1\frac{1}{2}$
Milling fineness, percent on 200-mesh sieve	6-8
Application thickness, mils	4-6

The specimens after dipping were dried at 230° F for 15 minutes, then fired for 4 minutes at 1550° F ($4\frac{1}{2}$ min for the heavier specimens of steel B). As soon as the specimens had cooled sufficiently for handling they were removed from the firing rack and quickly placed in the collection cell shown in figure 2. Joint A (see fig. 2) was sealed and the pressure in the cell was reduced by connecting through joint B to an 18-inch-diameter bell-jar reservoir which in turn was connected to an oil diffusion pump. The pressure in the bell jar before connecting in the cell was about 1×10^{-5} millimeter of mercury. After 2 minutes stopcock C was closed at which time the pressure in the collection cell had usually dropped to about 0.2 millimeter of mercury. The heater D was then energized and the temperature of the specimens raised to 338° F (170° C) in approximately 30 minutes and maintained at this value within ±4° F for 17 hours. This temperature was the same as that used by Darken and Smith (reference 10) for removal of hydrogen from steel. After cooling the system to room temperature a final pressure measurement was recorded, stopcock E was closed, and the inclined mercury manometer was disconnected from the system. The collection cell with the specimens still in position then served as a sample tube for the mass spectrometer.

In the mass-spectrometer analysis the collection cell was first connected into the analyzer through joint B. When the pressure in the analyzer had reached approximately 1×10^{-5} millimeter of mercury, stopcock C was opened. The analysis of the various gases was then made by recognized procedures. The final result showed the content of each gas present in the sample in mole percent. From these data the mole percent of deuterium in the total hydrogen gas was computed.

The volume of hydrogen gas at standard conditions per 100 grams of steel was computed from the following equation:

$$V = \left(\frac{Hv}{W}\right)\left(\frac{273}{760}\right)\left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right)$$

where W is the weight of the steel, H is the percent by volume of hydrogen in the gas, v is the volume of the cell not occupied by the specimens, P_2 is the final pressure in millimeters of mercury, P_1 is the initial pressure in millimeters of mercury, T_2 is the final absolute temperature, and T_1 is the initial absolute temperature.

METHODS OF INTRODUCING HEAVY WATER

In obtaining the data showing the relative importance of the several sources of hydrogen, the pickling treatment, the application of the enamel, the collection of gases after enameling, and the analysis of the gases with the mass spectrometer were all carried out in accordance with the standard procedures previously outlined. The only variation in these procedures came, for any given experiment, at that point in the process where it was necessary to substitute heavy water for regular water in order to evaluate the relative importance of a particular source. The following is a summary of the methods used to accomplish the substitutions. Only one substitution of heavy water for ordinary water was used in any experiment.

Acid pickling.- Heavy water was substituted for regular water in the 5-percent-sulphuric-acid solution. Deuterium sulphate, however, was not substituted for the sulphuric acid.[2]

Milling water.- Heavy water was substituted for the ordinary water used in preparing the enamel slip. The resulting slip was used within 48 hours after milling.

Quenching water.- A standard batch of the 109-0 frit was smelted by normal procedures in a small pot furnace. Part of this batch was quenched in regular water while a small part was quenched in heavy water. The part quenched in heavy water was then used in preparing the enamel slip.

Water in clay.- Only a few references could be found in the literature relative to methods for rehydrating clay from which the chemically combined water has been removed by heating. Most investigators who have accomplished the rehydration have used steam pressures of the order of 75 atmospheres. Schachtschabel (reference 11), however, reported that clay could be rehydrated if held at low pressures for long periods and this was the method adopted. The following procedure was used:

The Florida kaolin was first heated in shallow refractory boxes for 24 hours at 1000° F. This dehydrated clay was placed in platinum dishes and covered with heavy water. The dishes were then placed in an autoclave which contained additional heavy water and heated

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[2]Steel B, after the standard pickling treatment in the acid - heavy-water solution, was found to contain occluded hydrogen which consisted of 78 mole percent deuterium and 22 mole percent protium.

at 250 pounds per square inch (406° F) for 300 hours. The clay samples (a) before treatment, (b) after heating, and (c) after autoclaving were all examined by X-ray diffraction, by electron diffraction, and with the electron microscope. Weight-loss determinations were also made and these showed that the autoclave treatment accomplished an 80-percent rehydration of the clay molecule.[3]

Figure 3 shows the electron diffraction patterns and the electron micrographs. The electron diffraction patterns of untreated kaolin indicated a normal kaolinite structure while the heated sample gave a pattern typical of a dehydrated kaolinite. The rehydrated or deuterated clay, after removal from the autoclave, gave the normal kaolinite pattern but apparently had a smaller crystal size than the original material. This particular clay was unusual for a kaolin in that it showed small and poorly defined kaolinite crystals when examined with the electron microscope. A careful examination indicated practically no alteration in the appearance of the kaolinite fragments resulting from the dehydration. Thus, the dehydrated crystals may be considered as pseudomorphs of the original kaolinite. This observation is in keeping with the findings of Eitel, Muller, and Radczewski (reference 12).

When the Florida kaolin containing the heavy water was used in the preparation of the mill batch, the amount added was increased by the ratio 100:80 to compensate for the lower water content of the rehydrated clay.

Dissolved water in frit.- Although it is well-known that the dissolved water in glasses may be removed by melting in vacuum, insofar as could be determined, no one has attempted to resaturate a glass after removal of the water. The method devised by the present authors was as follows:

A 300-gram quantity of the normally smelted 109-0 frit was placed in a clay crucible which in turn was placed in the furnace shown by the schematic drawing in figure 4. A vacuum of 4 millimeters of mercury was applied and the crucible heated to 1850° F in 20 minutes. After 30 minutes in the temperature range of 1850° to 1875° F, the power was shut off and the furnace allowed to cool to room temperature. The vacuum was then released. After removal of the crucible, the frit was cracked away from the crucible and pulverized. This pulverized material

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[3]The heavy water content of the treated clay was obtained through analysis of a gas sample which was collected by heating the clay to 1000° F in a partial vacuum. The analysis showed that the water fraction contained 36.3 mole percent heavy water and 63.7 mole percent regular water.

was placed in platinum dishes and covered with heavy water. The dishes were then placed in an autoclave with additional heavy water and heated for 3 hours at 406° F (250 lb/sq in.). The material was then dried for several hours at 230° F after which it was quickly charged into a clay crucible maintained at 2150° F in an electrically heated furnace. After 15 minutes' heating, the crucible was removed from the furnace to cool in air. The resulting frit, which was practically bubble-free, was separated from the crucible material, crushed to pass through a 16-mesh sieve, and then used as the frit ingredient in the E-1 mill batch.

RESULTS

Table 4 gives the results of several blank determinations. Table 5 lists the total volume of hydrogen collected in each experiment per 100 grams of steel, the mole percent of deuterium in the hydrogen gas collected, and the relative importance of each source.

Figure 5 is a chart showing the mole percent of deuterium in the hydrogen gas collected from each of the several experiments. The values used in preparing this chart are the averages of the individual values for steel A and steel B.

CONFIRMING EXPERIMENTS

Fishscaling and Lifting

The results with deuterium as a tracer showed that the dissolved water in the frit was by far the most important source of defect-producing hydrogen. For confirmation of this finding, a second means of evaluating the effect of the dissolved water was believed desirable. The method used was to apply the 109-0 frit to steel specimens (a) in the normally prepared condition and (b) with the dissolved water entirely or mostly removed. After firing, the coated specimens were examined for lifts[4] and fishscales.

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[4]In this paper a lift refers to a visible separation of the enamel layer from the underlying metal. These lifts (light gray patches in figs. 6 and 7) are gas pockets of hydrogen that form between the steel and the coating layer. As more gas comes out of the steel with continued aging the pressure in the pocket increases until the point is reached where the enamel fractures. Other investigators (references 1 to 3) have demonstrated that the gas coming from the fracture, or fishscale, is mostly hydrogen.

It should be emphasized that in these experiments the frit as such was applied without the use of the customary clay, water, and other mill additions. This was accomplished by first dry grinding the frit and then suspending the resulting powder in water-free Ethyl Cellosolve. The suspension was applied by spraying. The specimens, after drying, were fired for the normal time (4 min for steels A and C and $4\frac{1}{2}$ min for steel B) at 1550° F.

When the frit as normally prepared was applied to specimens of steels A and B by this procedure pronounced lifting and fishscaling resulted. Figure 6(a) shows the appearance of the surface for steel A while figure 7(a) represents the appearance for steel B. Specimens of steel C showed no lifting or fishscaling when this same frit was applied.

Figures 6(b) and 7(b) represent specimens of steels A and B, respectively, coated with frit 109-0 that had been vacuum-melted to remove dissolved water. It is significant that no lifting or fishscaling is evident in either steel. Inasmuch as pronounced lifting and fishscaling occurred when the normally prepared frit was applied, whereas neither of these hydrogen defects appeared when the dissolved water was removed from the frit by melting in vacuum, it seems safe to conclude that the dissolved water in the frit was responsible for the defects in figures 6(a) and 7(a). This conclusion is further substantiated by figures 6(c) and 7(c). In this case, the 109-0 frit that had been melted in vacuum was rehydrated with heavy water[5] by the method previously outlined. The frit after this treatment again contained dissolved water and once again the pronounced lifting and fishscaling occurred.

In other experiments, an attempt was made to prepare the 109-0 frit in such a manner that it would initially contain little or no dissolved water. The raw batch materials were first weighed out and mixed and then slowly heated in a clay crucible to 500° F. After 20 hours at this temperature, which was believed sufficient to remove practically all of the water that was initially present in the raw materials, the mixture was charged without cooling into a crucible maintained at 2150° F in an electrically heated furnace. After a normal smelt, part of the batch was quenched on a heat-resistant alloy and the remainder was quenched in water. When the resulting frit was applied to the two steels, moderate lifting and fishscaling resulted. There was only a

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[5]The reason frit rehydrated with heavy water was used was because such frit was already available from earlier experiments.

small difference between the frit quenched in water and the frit quenched on the heat-resisting alloy, the former showing a somewhat greater number of defects. Specimens prepared from frit quenched in water are illustrated in figures 6(d) and 7(d). It will be noted that lifting and fishscaling are not so common as on the specimens prepared from the normally smelted frit (figs. 6(a) and 7(a)). These results indicated that the special smelting treatment resulted in a frit of reduced water content. On the other hand, it is obvious from the photographs that the special smelting treatment was not so effective in reducing the water content of the frit as was remelting in vacuum.

Reboiling

In the reboiling experiments frit 109-0 was prepared according to the formulation given in table 3 except that adherence oxides were added. After smelting, the frit contained 0.60 percent cobalt oxide and 1.94 percent manganese dioxide. Approximately 300 grams of this frit was then melted in vacuum with the same equipment and procedure as described earlier.

The resulting frit was dry-ground and applied to specimens of steels A and B by spraying from a Cellosolve suspension. After normal firing at 1550° F the specimens were placed over an oxygas flame and small areas heated beyond the reboil temperature (about 1050° F). Careful observation showed no reboil on either steel with this vacuum-melted frit while the untreated frit applied by the same procedure showed considerable reboil on steel B and slight reboil on steel A. When the vacuum-melted frit was prepared as a slip with clay and water and applied to the specimens, steel B showed slight reboil while steel A showed none.

DISCUSSION OF RESULTS

In the present study most attention was given to fishscales. It should not be inferred from this fact that the authors necessarily consider the other phenomena caused by hydrogen to be of lesser importance but rather that the experimental techniques were more adaptable to the fishscale type of defect. If reboiling rather than fishscaling had been used as a tool to determine the relative importance of the various sources of hydrogen, it is believed that the results would have been substantially the same. That such may be the case was demonstrated by the reboil experiments.

The fishscaling tests with deuterium used as a tracer showed the dissolved water in the frit to be the principal source of hydrogen

evolved from the coated steel. According to this finding, avoidance of the dissolved water in the frit should eliminate most of the hydrogen from the system and thus make it possible to prepare specimens that would not reboil. Tests described in this paper showed this to be the case.

The method devised for collecting the gas given off during fish-scaling gave samples that were diluted both with residual air and with gases released by the enamel and by the Pyrex glass surfaces of the collection cell. In table 4 only the evolved gases are listed; nitrogen and oxygen were assumed to have originated from residual air and are not included in the analyses. The table shows that the absorbed gas given off at 338° F by the glass surfaces of the collection cell was very small. The gas consisted mostly of water. With chips of coating material in the cell, water vapor was again the principal gas but the carbon-dioxide content increased. A trace of hydrogen was also present.

In the tracer experiments, summarized in table 5, residual air and absorbed gases were also present to dilute the sample. The important data in these tests, however, were the mole ratio of deuterium to protium and this ratio was not affected by the dilution.

The finding that the dissolved water in the frit is the major source of hydrogen is in keeping with the belief of Hoff and Klarding (reference 13). It also agrees with what might be predicted from the work of Miller and Sweo (reference 14), who experimented with fused masses of iron powder and porcelain enamel constituents. These authors found that partial removal of the dissolved water from the frit by heating in dry nitrogen to 350° C (662° F) decreased the gas (hydrogen) entrapped in the fused mass. The same authors also reported that the water removed by the dry nitrogen treatment was 0.30 percent by weight. This is equivalent to 372 cubic centimeters of water vapor at standard conditions per 100 grams of frit. Dalton (references 15 and 16) reports a maximum of 94 cubic centimeters per 100 grams for borosilicate glasses as determined by the vacuum fusion method, while the maximum reported by Hahner, Voight, and Finn (reference 17) for borosilicate optical glasses was 49 cubic centimeters per 100 grams of glass.

Dalton (reference 15) states that borosilicate glasses as a class contain more water than nonborosilicates. Ground-coat enamels are normally higher in boron oxide than borosilicate glasses, hence it is conceivable that ground-coat enamels could contain appreciable amounts of water. The data of Miller and Sweo (reference 14) point in this direction.

Calculations show that the total amount of enamel on the 10 specimens of steel A during any one experiment averaged about 6.5 grams. Assuming the water content of the enamel to be 0.3 percent by weight,

24 cubic centimeters of hydrogen could be formed if all of the dissolved water reacted with the steel. The fact that the maximum amount recovered in any of the tests was 0.8 cubic centimeter indicates the possibility that only a small part of the dissolved water reacts with the steel during a normal firing. Additional reaction could occur on successive firings and during each of these firings the steel could become recharged with hydrogen. Thus, reboiling might be expected to occur after each successive firing until the water content of the enamel had been depleted by reaction with the steel. King (reference 18) found that after 23 to 25 heatings no further reboil took place. He also found if a ground-coated specimen is fired in vacuum, it will not reboil in any subsequent firing. These results as well as the reboil experiments reported in this paper indicate that the dissolved water in the enamel is the major source of the hydrogen responsible for reboil.

Determination of the water content of the various frits was beyond the scope of this investigation. It was hoped that the vacuum melting would remove practically all of the original water from the 109-0 frit, and that the autoclave treatment followed by rapid melting would successfully restore a comparable number of moles of deuterium oxide. Figures 6 and 7 show a comparable degree of lifting and fishscaling for the frit that had been rehydrated after vacuum melting and for the normal 109-0 frit. This would indicate that the water contents of the two frits were of the same general order of magnitude but gives no indication whether the regular water had been completely replaced with heavy water. That such a replacement may not have been accomplished is indicated by the data listed in table 5. These data show the pickling treatment, the milling water, and the clay to be very minor sources of hydrogen and of little significance when compared with the dissolved water in the frit. If this is the true picture then, when a frit was used in which regular water was replaced by heavy water, the resulting gas sample should have shown the hydrogen to consist almost entirely of the deuterium isotope. Actually, in the two experiments performed with the deuterated frit the mole percent of deuterium was 53.5 and 52.9. These results imply that the water in the frit had not been completely replaced with deuterium oxide.

To investigate whether such was the case, a sample of the deuterated frit was melted in vacuum in a closed system that had previously been degassed. A sample of the resulting gas was then reduced by use of a hot tungsten filament. This reduction was necessary because the mass spectrometer does not readily separate the two isotopes when they are present in the form of water. After the reduction only traces of water remained, the sample consisting, for the most part, of protium, deuterium, and carbon monoxide. The mass-spectrometer analysis when converted back to water, heavy water, and carbon dioxide

showed the following mole percentages of these constituents in the deuterated frit:

H_2O	46.3
D_2O	37.7
CO_2	16.0

One explanation for this unexpectedly high content of regular water in the deuterated frit is the possible presence of residual water in the frit after the vacuum melting. Figures 6 and 7 show that the 109-0 frit when melted in vacuum did not cause lifting or fish-scaling when applied to steels A and B. This implies a large reduction in the dissolved water content but does not necessarily prove that all of the dissolved water had been removed. There may be a critical value below which the water or hydroxyl group is so tightly bound in the glass structure that no reaction will occur with the steel during the firing process. When deuterium oxide was introduced, the water content as such increased and the deuterium oxide became diluted by the residual water present in the sample.

Regardless of the contamination of deuterium oxide with residual water, the experiments showed the predominant importance of the dissolved water in the frit as compared with the other sources of defect-producing hydrogen that were investigated. In view of recent work on hydrogen in steel, this finding is not surprising. Darken and Smith (reference 10) found that heating at 170° C (338° F) removed 90 percent of the hydrogen that had been introduced into the steel during acid pickling. Thus, practically all of the hydrogen initially present in the steel, as well as that introduced during cleaning operations, would be expected to leave the steel before the enamel fuses over. Hydrogen introduced at firing temperatures, on the other hand, has a tendency to remain in the steel. Smith (reference 4) states that there is a possibility that metal which has been saturated at high temperatures may retain extra hydrogen, over and above the saturation limit (see fig. 1), if it has been rapidly cooled. Smith also states that this seems to occur in the case of iron.

A retention of this type is in keeping with the findings of Davis, Keeler, and Chu (reference 19). These authors found that when a ground-coated specimen was cooled slowly by any of several prescribed schedules no lifting or fishscaling resulted. When coated specimens are cooled slowly, they believe that the hydrogen comes out of the steel to react with iron oxide at the interface forming water and reduced iron, and that the water in turn is dissolved by the enamel glass. They infer that this reduction reaction and the solution of the resulting water into the glass structure may occur at temperatures as low as 392° F. The results of the present study with enamel applied to the

nonfishscaling titanium-bearing steel indicate that such a hypothesis is unnecessary inasmuch as table 4 shows that hyrogen is capable of diffusing through the glass layer at temperatures as low as 338° F. An additional test was made in which coated specimens of steel B were placed in the collection cell while still hot. Practically no lifting or fishscaling resulted, yet a normal quantity of hydrogen was collected, again demonstrating that hydrogen is capable of diffusing through the glass under these conditions. Reports in the literature that hydrogen will not diffuse through glass in any significant quantity at such low temperatures (reference 20) refer to molecular hydrogen. It should be pointed out, however, that in the enamel-steel system, the hydrogen diffusing through the enamel layer might be in the atomic or possibly even the ionic state.

Several authors (references 14 and 19) have ascribed considerable importance to the chemically combined water in the clay used for suspending the enamel slip. The present work indicates that the clay is only a minor source of hydrogen. The chemically combined water is released by the clay molecule at temperatures as low as 1000° F and, if the enamel is applied at a normal thickness, the water may be mostly expelled before the enamel fuses. Before fusion the enamel structure is open and the steam that evolves from the clay escapes into the furnace atmosphere with very little chance of a high concentration at the steel surface. The large effect of clay noted by Miller and Sweo (reference 14) could have been due to the relatively large mass of their samples. In their work, the enamel undoubtedly fused before the clay molecule was completely dehydrated.

The water taken up by the enamel during milling is shown in table 5 and figure 5 to be of minor importance. The water that is picked up is possibly present as a thin gel film around each frit particle. This gel would become dehydrated in the early stages of firing without contributing significantly to the dissolved water content of the frit.

It was expected that the quenching water would have a larger effect than was actually found. The pouring of the molten glass into cold water should present ample opportunity for water absorption. The finding that this operation was of minor importance indicates that the molten glass may not be in contact with water for a sufficient time to absorb any appreciable quantity of water. If the glass was completely free of dissolved water at the time of pouring, however, the effect of the quenching water might be more pronounced.

In considering these data, it should be pointed out that according to the outlined procedure each variable was introduced into a system that already contained all of the other possible sources of hydrogen. For example, when the deuterated clay was introduced, regular hydrogen could have been contributed in the same experiment not only by the

dissolved water in the frit but also by the quenching water, the milling water, and the pickling acid. This procedure was selected in order to obtain an estimation of the relative importance of the various sources. If a water-free frit had been used, however, the results might have been entirely different. For example, the present work shows clay to be of minor importance. If, on the other hand, the clay had been introduced to a system containing a frit free of dissolved water, then it is conceivable that the unsaturated frit could have a strong affinity for any water with which it came in contact. Under such conditions, the water given off by the clay might be assimilated by the semimolten frit and this water could in turn react with steel at the higher temperatures to form hydrogen. That some such mechanism might be active, was indicated by the reboil experiments. When steel B was coated with frit 109-0 that had been melted in vacuum no reboiling occurred. Yet, when clay was added to this same frit and the batch milled with water, reboiling did occur. These results would indicate that if an enamel is desired that is completely free of reboil and fishscaling tendencies, it may be necessary to remove all water from the system whatever its source.

Table 2 shows no hydrogen in steel C (titanium bearing) as received. This observation of itself does not prove that hydrogen cannot enter the structure of a titanium-bearing steel. It may mean only that this particular steel has an open rift structure. Because of this structure, the hydrogen that enters the steel at elevated temperatures may come out readily during cooling rather than becoming dammed up in "lake rifts" of the types postulated by Davis, Keeler, and Chu (reference 19). That some hydrogen is introduced into the titanium-bearing steel during enameling operations is evident from the data in table 4, although the quantity of hydrogen expelled during the treatment at 338° F was much less for steel C than that given off by the two low-carbon steels A and B (see table 5).

The attempt to prepare a water-free frit by using dehydrated raw materials and smelting in an electric furnace was not completely successful. Some water may have been introduced into the frit through traces of residual water in the "dried" raw materials or through traces of water vapor in the atmosphere of the smelting furnace. Sufficient improvement was noted, however, to indicate that a method of this type shows promise.

The desirability of using a ground-coat frit free of dissolved water is believed obvious. The present data indicate that a coating prepared from such a frit and with all other water removed from the system should be free of reboil, fishscaling, and possibly primary boil. The use of a titanium-bearing steel appears to eliminate reboil and fishscaling, but primary boil if it is caused by hydrogen would be expected to occur in titanium-bearing steel just as it does in the others. The use of a water-free enamel should help materially to

eliminate hydrogen-caused defects not only with porcelain enamels but also with vitreous-type ceramic coatings. In ceramic coatings complete coverage is of course essential for the optimum protection of the metal.

CONCLUSIONS

The relative importance of various sources of defect-producing hydrogen in the enameling process was determined by tracer experiments with a selected ground-coat enamel applied to several low-carbon steels. Additional experiments in which the presence or absence of lifting, fishscaling, and reboiling served as criteria confirmed the tracer work in general. From the results of this investigation, the following conclusions may be drawn:

1. At the conditions investigated, dissolved water in the frit is the principal source of defect-producing hydrogen.

2. In normal enameling operations, chemically combined water in the clay, milling water, quenching water, and acid pickling are minor sources of hydrogen. However, if frit free of dissolved water is used, these sources may increase in importance.

National Bureau of Standards
Washington, D. C., July 12, 1951

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TABLE 1

CHEMICAL ANALYSES OF THREE STEELS

Steel	Description	Source of analysis	Analysis in percent by weight of -				
			C	P	S	Mn	Ti
A	Enameling iron	(1)	0.012	0.005	0.025	0.017	----------
B	Fishscaling steel	(2)	.033	.003	.010	(3)	----------
C	Ti-bearing steel	(4)	.09	.040	.050	.50	0.2 to 0.5

[1]Representative analysis from Metals Handbook, Am. Soc. Metals (Cleveland), 1948, p. 424.

[2]Analysis by Analytical Chemistry Section of NBS.

[3]Not determined.

[4]Nominal analysis listed by Inland Steel Co. in advertising literature published in 1949.

TABLE 2

GAS CONTENTS OF THREE STEELS

Steel	Description	Gas content by vacuum fusion[1] in -					
		Weight percent			Cm^3 per 100 grams of steel		
		O_2	N_2	H_2	O_2	N_2	H_2
A	Enameling iron	0.0718	0.0073	0.00035	50.2	5.8	3.9
B	Fishscaling steel	.0215	.0053	.00014	15.0	4.2	1.6
C	Ti-bearing steel	.0047	.0333	Nil	3.3	26.6	Nil

[1]Determined by Chemical Metallurgy Section of NBS.

TABLE 3

BATCH AND COMPUTED OXIDE COMPOSITIONS

OF 109-0 FRIT

(a) Batch composition.

Constituent	Parts by weight
Potash feldspar	30.82
Borax (hydrated)	44.25
Flint	30.50
Soda ash	9.16
Soda niter	5.15
Fluorspar	8.30
	128.18

(b) Computed oxide composition.

Oxide	Percent by weight
SiO_2	51.0
B_2O_3	16.1
Al_2O_3	5.7
Na_2O	15.4
K_2O	3.5
CaF_2	8.3
	100.0

TABLE 4

VOLUME OF GAS COLLECTED AND ANALYSES OF EVOLVED GASES FROM DETERMINATIONS MADE WITH COLLECTION CELL EMPTY, WITH SPECIMENS OF COATED STEEL C IN CELL, AND WITH CHIPS OF COATING MATERIAL IN CELL

Test	Material in collection cell	Volume of gas collected at 338° F	Analysis of evolved gas (mole percent)		
			H_2	H_2O	CO_2
1	None - cell empty	Trace	0	98.7	1.3
2	Steel C with coating E-1	[a]0.02	45.5	52.3	2.2
3	[b]Coating chips	Trace	.4	80.2	19.4

[a] Cm^3 of gas per 100 grams of steel.

[b] Same total weight of E-1 coating as was present on specimens in test 2. Coating chips were obtained by flexing specimens of steel C immediately after firing.

TABLE 5

VOLUME OF HYDROGEN GAS COLLECTED AT 338° F, MOLE PERCENT OF DEUTERIUM IN HYDROGEN, AND RELATIVE IMPORTANCE OF INVESTIGATED SOURCES OF DEFECT-PRODUCING HYDROGEN IN STEEL

Source investigated	Steel base	Volume of hydrogen collected (cm^3/100 grams of steel) (1)	Deuterium in hydrogen (mole percent)	Relative importance of source (2)
Pickling acid	A	0.37	0.1	4
	B	(3)	.5	
Milling water	A	.24	.1	5
	B	.32	.1	
Water in clay	A	.25	.2	3
	B	.28	.8	
Quenching water	A	.80	.5	2
	B	.20	1.5	
Dissolved water in frit	A	.56	53.5	1
	B	.44	52.9	

[1]Computed from change in pressure in collection cell after 17 hrs at 338° F and from hydrogen content of collected gas. Values are for gas at standard conditions.

[2]Number 1 refers to most important source and number 5 to least important source.

[3]Through a misunderstanding, only the protium-to-deuterium ratio was determined on this sample, making it impossible to calculate the volume of hydrogen collected.

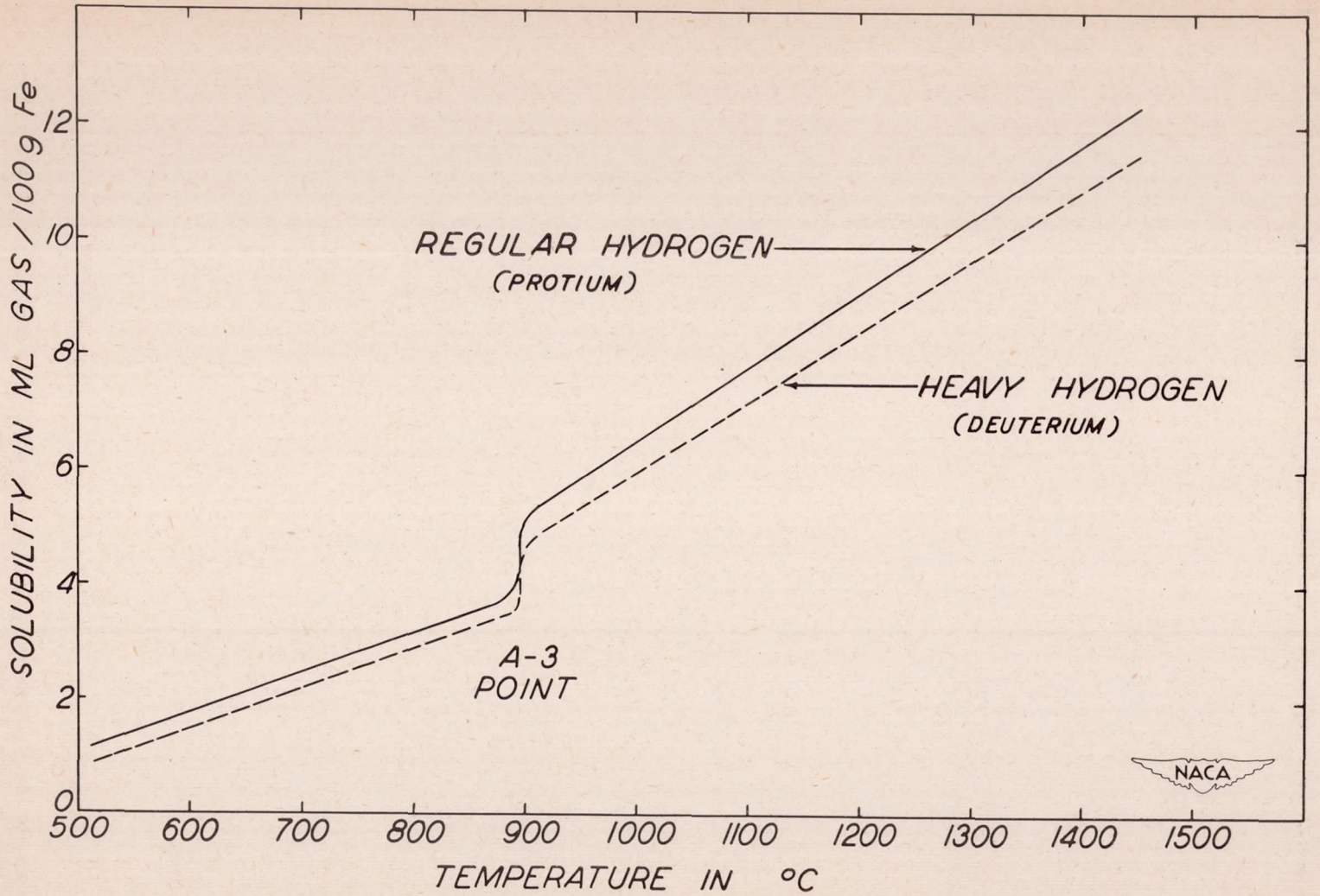


Figure 1.- Solubility-temperature curves for regular hydrogen and heavy hydrogen in ingot iron at atmospheric pressure as determined by Sieverts, Zapf, and Moritz (reference 6).

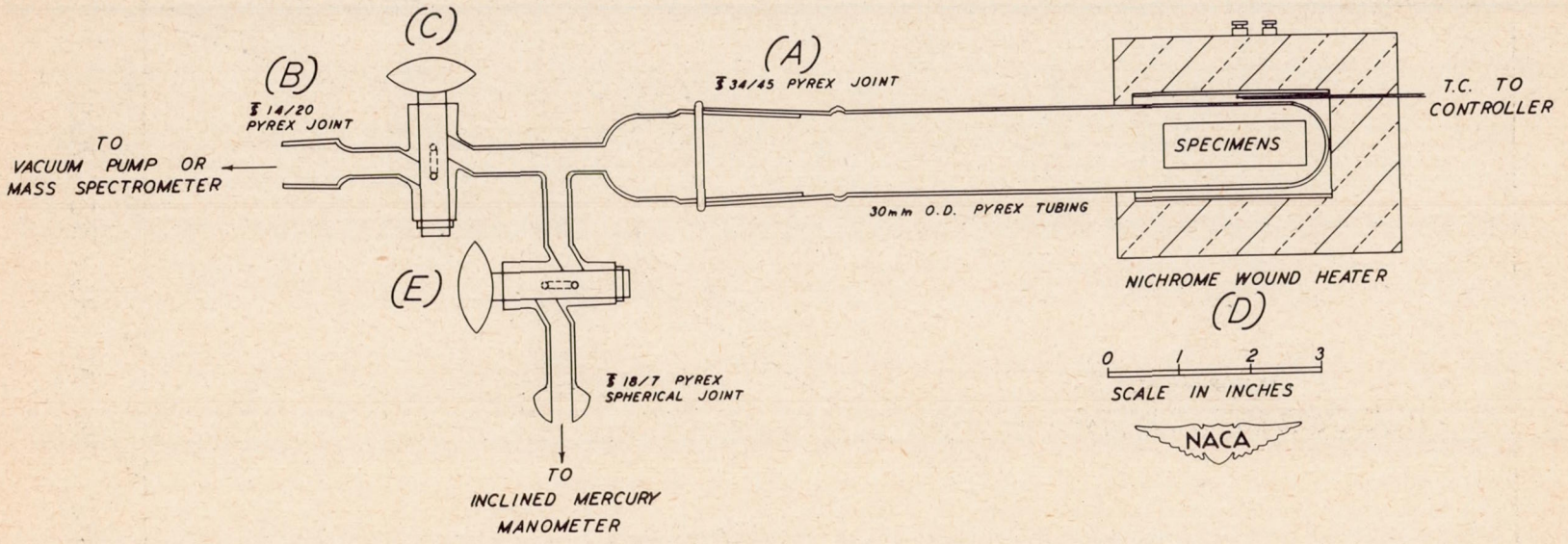
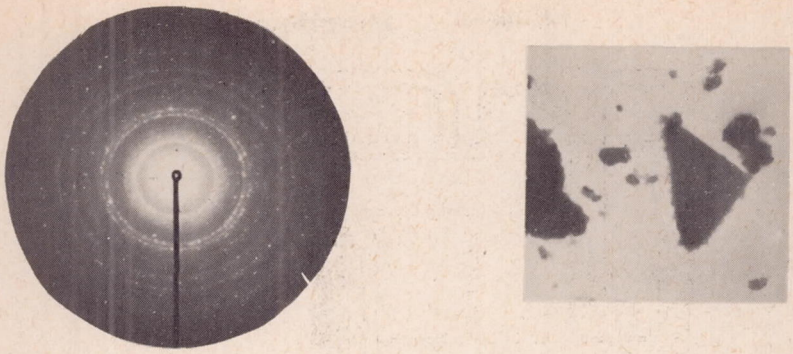
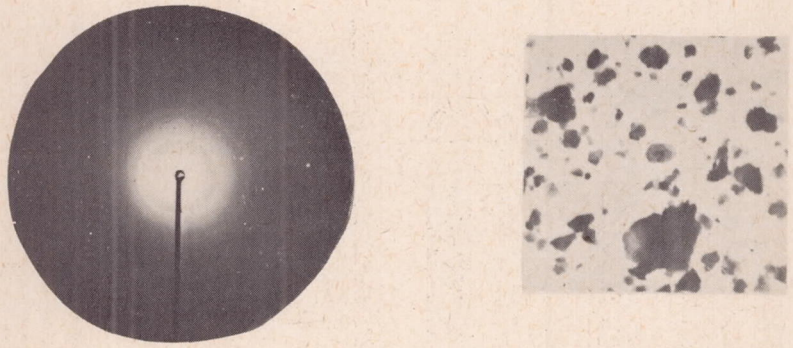


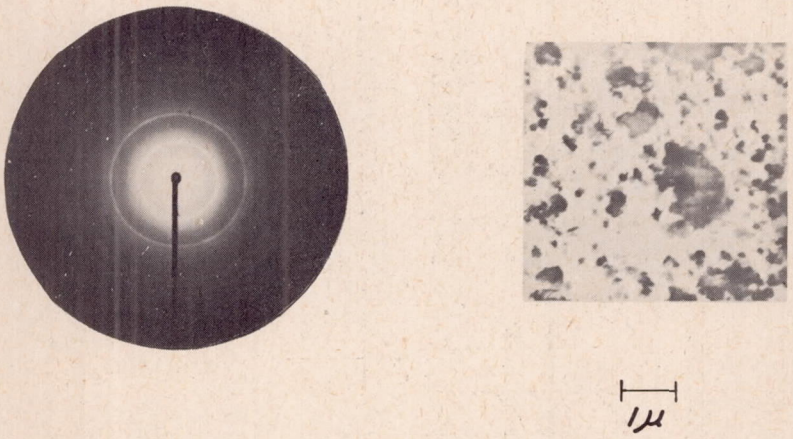
Figure 2.- Schematic drawing of collection cell.



(a) No treatment.



(b) After heating at 1000° F for 48 hours.



(c) After autoclaving dehydrated material for 300 hours at 250 pounds per square inch with heavy water.

Figure 3.- Electron diffraction patterns and electron micrographs of Florida kaolin.

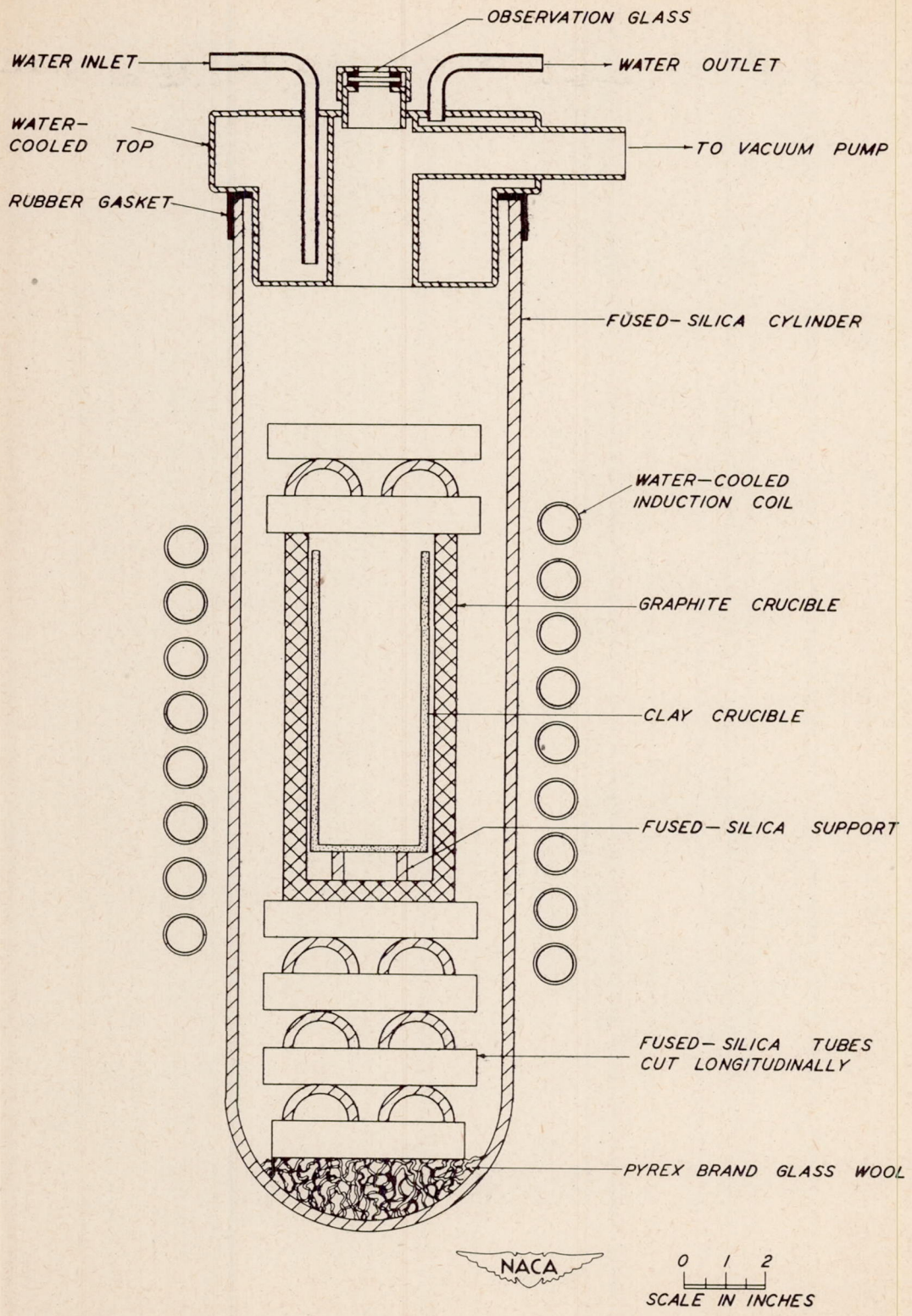


Figure 4.- Schematic drawing of vacuum melting furnace used for removing dissolved water from normally prepared frit.

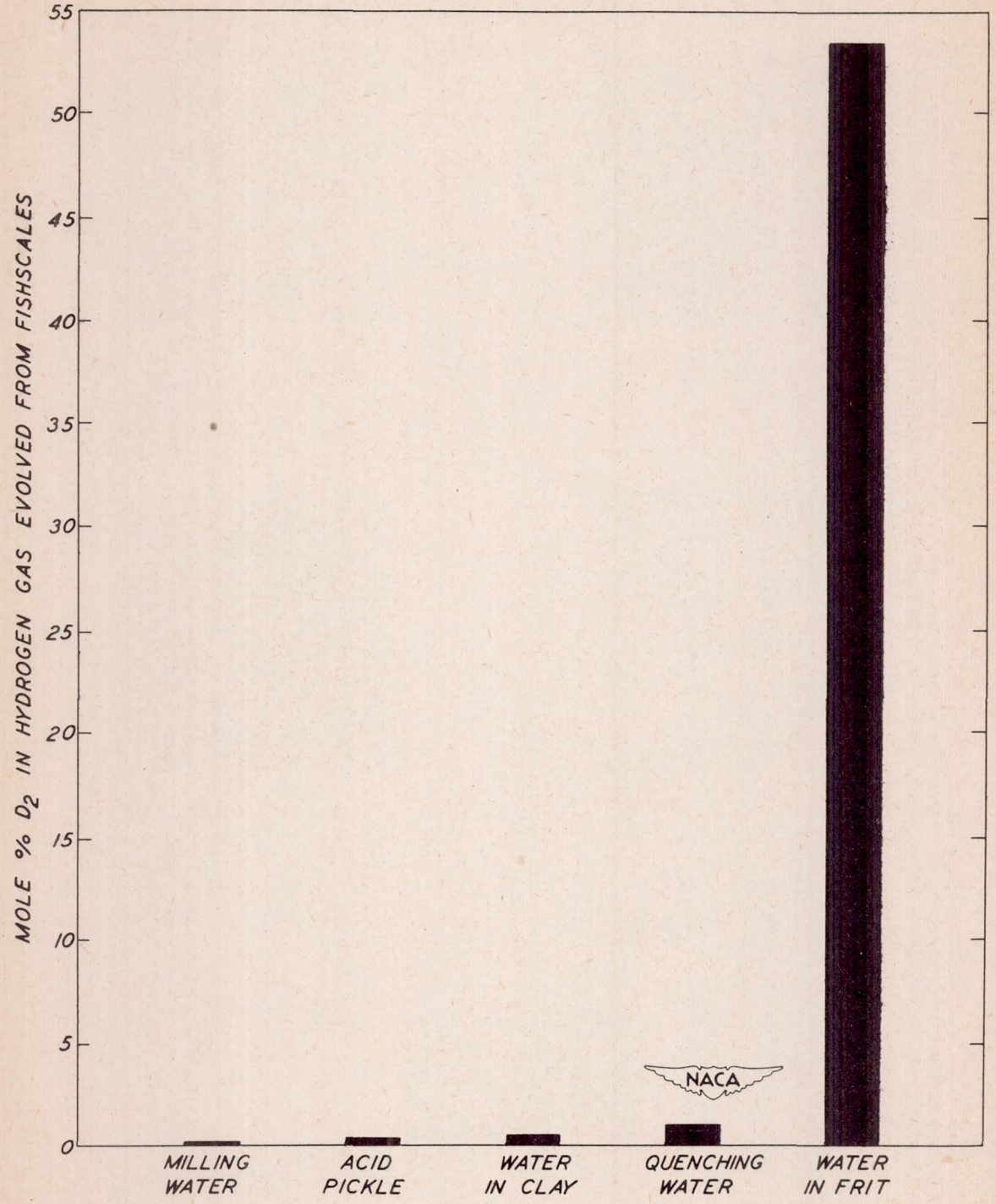
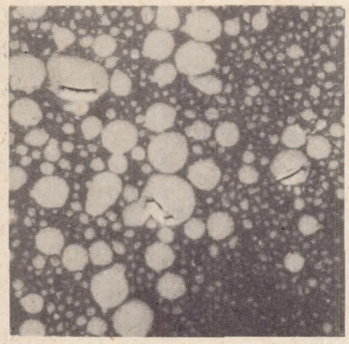


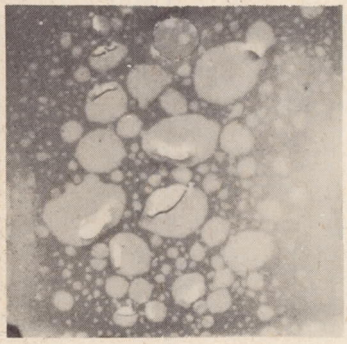
Figure 5.- Mole percent of deuterium in hydrogen (protium plus deuterium) evolved from ground-coated steel specimens. Experiments were designed so that heights of columns indicate relative importance of listed coating processes as sources of defect-producing hydrogen in steel.

STEEL A

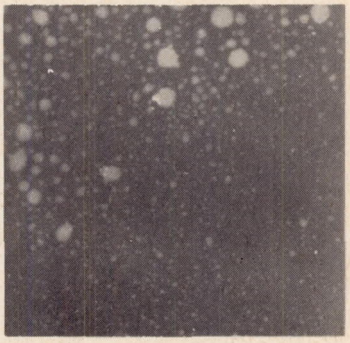


(a) Normally prepared frit.

(b) Same frit as shown in (a) after vacuum melting to remove dissolved water.

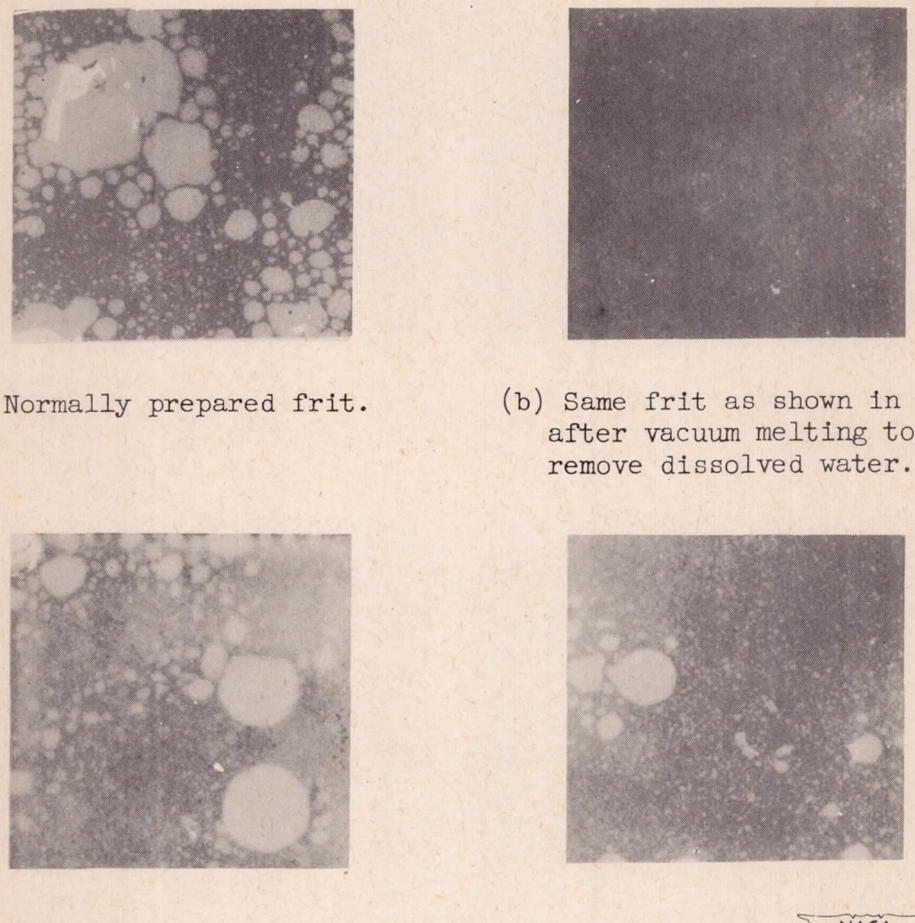


(c) Vacuum-melted frit that was subsequently autoclaved with heavy water and then remelted.



(d) Same frit as shown in (a) except prepared from dehydrated raw materials and melted in electric rather than gas-fired furnace.

Figure 6.- Specimens of enameling iron (steel A) coated with a ground-coat frit containing no adherence oxides. Light areas are separations at interface caused by hydrogen evolution.



(a) Normally prepared frit.

(b) Same frit as shown in (a) after vacuum melting to remove dissolved water.

(c) Vacuum-melted frit that was subsequently autoclaved with heavy water and then remelted.

(d) Same frit as shown in (a) except prepared from dehydrated raw materials and melted in electric rather than gas-fired furnace.

Figure 7.- Specimens of low-carbon fishscaling steel B coated with a ground-coat frit containing no adherence oxides. Light areas are separations at interface caused by hydrogen evolution.

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